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# LABORATORY GUIDE FOR THE IDENTIFICATION OF PETROLEUM PRODUCTS

Fred K. Kawahara

Federal Water Pollution Control Administration
Cincinnati, Ohio

January 1969

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Federal Water Pollution Control Administration
Division of Water Quality Research
Analytical Quality Control Laboratory
Cincinnati, Ohio

CLEAN WATER

# LABORATORY GUIDE FOR THE IDENTIFICATION OF PETROLEUM PRODUCTS
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# Laboratory Guide for the Identification of Petroleum Products

by

Fred K. Kawahara, Ph.D., F.A.I.C.

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Federal Water Pollution Control Administration
Division of Water Quality Research
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# Laboratory Guide for the Identification of Petroleum Products

by

Fred K. Kawahara, Ph.D.

## INTRODUCTION

Oil pollution has become a major problem in the coastal and surface waters of the United States and many other countries. Oil discharges and spills from industrial plants and commercial ships produce unsightly and unhealthy conditions which ruin beaches and recreational areas, impart unpleasant taste and odor to water, and in many cases result in harm to fish and other aquatic life. Larger oil spills will occur more frequently as the demand for petroleum products becomes greater and ocean oil transports become larger.

The urgency of the problem requires that detailed analytical procedures be developed to detect and identify petroleum pollutants, in order to establish responsibility for violations of water quality standards and to secure abatement of the pollution.

Many oil spills occur without eye witness. In such cases technical information and data will be necessary to facilitate locating and identifying the sources of the pollution, created by petroleum products. Following identification, proper enforcement for control procedures may then be exercised.

This laboratory guide for the identification of petroleum pollutants has been prepared to provide the analyst with specific methods leading to a positive characterization of the waste material.

## SAMPLING

### Collection

Oily materials may be collected from the surface of the water by means of three devices. The first is a glass, wide-mouth filtering funnel, connected by teflon tubing to a two-way stopcock. Volatile oil product found upon the water surface is ladled with the aid of this device; the lower water phase is discarded by opening the stopcock. The upper petroleum phase is transferred to a large container. Ladling and water-discard operation should be repeated until a sufficient amount of oil (10 grams or more) is collected.

An alternative collector is a paint-free dustpan with a suitable stopcock attached to the handle. Collection and concentration of several grams of petroleum product can be achieved with this household device. Heavy, viscous material, such as asphalts, can be collected in a similar manner. Transfer to the final collecting jar from the funnel, jar, or dustpan, is possible with aid of a clean spoon or stick.

The third device is a large household mop with a ringer attachment. It is suggested that, before use, the sponge, whether derived from

natural or synthetic materials, be rinsed thoroughly with a proper solvent, such as chloroform. This mop is passed through the oil pool; the absorbed materials are squeezed out and transferred by means of a funnel into the collecting jar. The sampling operation is facilitated by attaching the bottle, scoop, or mop to a long pole. Where possible, reference samples of oil should also be obtained from vessels or shore facilities.

Preservation of Samples

The samples containing oil and water are protected against autoxidation (15) and other chemical conversions by removal of air and exclusion of light. Carbon dioxide may be used to displace air. If dry ice is available, a piece (approximately 0.5 cu inches) may be added to the sample. As soon as the effervescing has stopped, the jar is sealed with a teflon lined cap. The bottle is not capped if unused portions of solid dry ice are visible. Samples should be preserved in the refrigerator whenever possible.

When nitrogen or an inert gas is not available, the sample bottle is filled carefully to the top with water to displace air.

Sample Preparation for Analyses

To prepare a volatile petroleum sample for analysis, the water sample is extracted with distilled pentane or, if necessary, with purified dichloromethane or chloroform. To a 500 ml separatory funnel

200 ml of pentane is added. A portion amounting to about one-half gram to five grams of petroleum pollutant is added to the pentane solution. The extent to which the petroleum material dissolves in the pentane is observed. Dichloromethane or chloroform is used, if necessary, to dissolve the pollutant. The separatory funnel is tilted back and forth for one minute to extract the product. The funnel is set on a ring stand and is placed under a well ventilated hood.

After the lower phase is drawn off, the 200 ml pentane extract containing the petroleum pollutant is washed once with 10 ml of distilled water, and the lower aqueous layer is drawn off. (For the dichloromethane system, the aqueous layer will be on top.)

The extract layer is then dried by permitting the solvent mixture to pass dropwise through 5 grams of anhydrous sodium sulfate held in a No. 12 folded filter paper seated on a filtering funnel with a 75 mm diameter and 75 mm stem. The filtered, pollutant extract is collected in a 300 ml round-bottom flask equipped with a standard taper 24/40 ground-glass joint.

If the petroleum product is thought to be less volatile than gasoline or kerosene, chloroform should be used as the extracting solvent. Thus, greases, asphalts, residual oils, etc., are extracted with chloroform; the extract is washed with distilled water and is dried over anhydrous sodium sulfate prior to the concentration step.

Concentration

For the removal of pentane or chloroform, the distillation apparatus, similar to that suggested by Fieser (10) is used. A modified Pauly (22) receiver, made from a 125 ml Erlenmeyer flask, is attached to the adapter which follows the water condenser. Another modification is the use of 19/38 standard taper ground-glass joints at all connections except the Claisen distilling head which is fitted with a 24/40 standard taper joint. The distillation flask is fitted to the Claisen head by means of a ground-glass joint. The Claisen head is equipped with an ebullating tube through which the nitrogen gas is bled slowly, and the ebullating tube is fitted with a 10/30 standard taper joint. A thermometer well is fitted at the outlet of the Claisen head.

The Pauly receiver (22) is connected by means of a foot-long suction tubing to a dry ice trap, which is fitted with an inlet and outlet exhaust gas stopcock. The exhaust gas stopcock is connected to a mechanical vacuum pump or line. Heat is provided by a thermostatted water bath. Extracting solvent (pentane, dichloromethane, or chloroform) is removed with aid of vacuum, from the laboratory vacuum line or a high vacuum mechanical pump.

When the pollutant is considered to be a petroleum product other than crude, naphtha, gasoline or jet fuel, it is recommended that the solvent mixture containing the volatile pollutant be subjected to the milder atmospheric distillating condition. Table I shows the high volatility of some of the petroleum products.

Table 1. Properties of Petroleum Products[9], a

| Material | Crude | High Gravity Naphtha | Low Gravity Naphtha | Gasoline | Jet Fuel | Kerosene | Gas Oil | Paraffin Wax | White Oil | Cutting Oil | Motor Oil | Fuel Oil #1 | Fuel Oil #2 | Fuel Oil #4 | Fuel Oil #5 | Grease | Fuel Oil #6 | Asphalt & Feed Stock |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Gravity, API | 13.5 to 33.5 | 45 to 75 | 30 to 53 | 58 to 62 | 40 to 55 | 40 to 48 | 30 to 33 | 34 to 39 (as molten wax) | 29 to 32 | | 24 to 30 | >35 | >28 | 9 to 36 | 0.5 to 24 | | +5 to 23 | -8 to 18 |
| Sulfur | 0.3 to 4.0% may be sour | 0.02% | 0.02% | <0.25% | <0.10% | <0.1% | 0.2 to 2.0% | | | | High | 0.1 to 0.5% | 0.2 to 1% | 0.2 to 2% | 0.2 to 4.6% | High | 0.3 to 5.25% | High |
| Distillation i.B.P. | 40°F | 95°F | 160°F | 90°F | 100°F | 355°F | 400°F | ca. 430°F-5% | | | ca. 640° | 360°F | 370°F | ca. 420°F | | 415°F | 492°F | >>500° |
| e. P. | +850°F | 206°F | 410°F | 408°F | to 500°F | to 575°F | 800°F | 60 to 90% at 620°F | | | 879° | 625°F | 675°F-90% | 681°F | | 480°F for tube oil | 1264°F | >1300° |
| Melting Point | | | | | | | | 147°F to 196°F | | | | | | | | | | |
| Molecular Weight | | | | 72-170 | 100-220 | 156-226 | 212-294 | 530 to 610 | | | 248 to 492 | | | | | | | |
| Comments | | | | lead alkyls bromine chlorine (infrequently lead-free) (phosphorus or boron =10%-20% of lead value) | | | | Paraffinic | Colorless (or nearly) Highly paraffinic | Glycerides Chlorine 0.0 to 1% Sulfur 0.2 to 1% Metallic soaps(?) and mineral oil | Phosphorus 1 part Sulfur 2 part Zinc 1/2 part (other additives) | | | | | Lithium soaps Barium " Calcium " Sodium " Zinc " Lead " Diesters | Flash Carbon Asphaltenes Ignition Quite flexible No hydrolysis | |
| Kinematic Viscosity 100°F Centistokes 210°F | ca. 2.3 to 10.5 | | | | | | | | | | | 1.4 - 2.2 | <4.3 | 5.8-24.0 | 24.1 min. 92 max. | | 92-630 | |

Footnote: (a) a portion of this table is from reference 9

Volatile solvents and petroleum products are recovered in the Pauly receiver or in the dry ice trap. Distillates are analyzed to determine the presence of material other than the extracting solvents. The refractive index of the extracting solvent should be determined prior to the extraction procedure, using an Abbe refractometer.*

During the final stages of concentration, the concentrate is transferred to a 25 or 50 ml flask. The removal of the solvents concentrates the oil pollutant into a small volume.

An alternative method for preparing the sample for analysis is separation by centrifugation. This method is suitable for large volumes of liquid petroleum pollutants admixed with water. However, the removal by centrifugation of traces of water from the viscous material or from minor amounts (0.1 gram) of actual liquid sample is difficult. The extraction procedure is therefore recommended in these instances.

## PRELIMINARY SOLUBILITY STUDIES

In spite of the complex structures of petroleum products it is possible to make some reasonable prediction as to product type by observing the behavior in organic solvents. This preliminary observation is especially useful for identifying the heavier petroleum products.

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*Mention of products and manufacturers is for identification only and does not imply endorsement by the Federal Water Pollution Control Administration, U. S. Department of the Interior.

From the thoroughly dried residue, free of water and extracting solvent, a 0.2 gram portion is taken and placed into a 20 ml vial. Seven ml of hexane is added and the mixture is stirred with a spatula. The solubility of the residue is observed in this solvent. This test is repeated to determine solubility in diethyl ether and in chloroform. If the material is soluble in each of the three solvents in the cold, the material can be assumed to be one of the following: light or heavy naphtha, kerosene, gas oil, white oil, certain types of cutting oils, motor oils, paraffin, diesel oil, or jet fuel.

Vaseline or white petroleum jelly is only partly soluble in hexane, in ether, and in chloroform. Thus, vaselines are unique. However, greases, heavy residual oil (#6) and asphalt (feed stocks) are insoluble in hexane and in diethyl ether, but are readily soluble in chloroform.

These solubility characteristics of petroleum materials are summarized in Table II.

Table II. Solubility of Petroleum Products

| Product | Hexane | Ether | Chloroform |
|---|---|---|---|
| Light naphtha | VS | VS | VS |
| Heavy naphtha | VS | VS | VS |
| Gasoline | VS | VS | VS |
| Jet fuel | VS | VS | VS |
| Kerosene | VS | VS | VS |
| Gas oil | VS | VS | VS |
| Diesel oil | VS | VS | VS |
| White oil | VS | VS | VS |
| Cutting oil | S | S | S |
| Motor oil | S | S | S |
| Paraffin wax | S | S | S |
| White petroleum jelly | PS | PS | PS |
| Grease | I | I | S |
| Residual fuel oil | I | I | S |
| Asphalt feed stock | I | I | S |

The solubility behavior of 0.2 gram of material was observed in 7 ml of the cold organic solvent.

## SEPARATION, ANALYSES, AND CHARACTERIZATION

The remaining dried residue obtained from the concentration step is divided into two portions. One portion is used to determine the API gravity, infrared spectra, and molecular weight. With care, the residue may be recovered. The other portion is used to determine the sulfur value, distillation range, and viscosity or refractive index. For subsequent identification, the gas chromatographic analyses of the more volatile petroleum products and the infrared analyses of the less volatile products will be performed.

After the solubility behavior has been determined, the data of Table I and II are consulted for guidance.

### Determination of API Gravity

The analyst is referred to ASTM D 287 (1) for determining the API gravity by means of the hydrometer. If the sample size is limited, the density may be measured by the pycnometric methods, ASTM D 941 and ASTM D 1217 for liquids. The density is referred to 60°F. Then, degrees API = $\frac{141.5}{\text{sp. gr.}} - 131.5$. If sufficient liquid is available, the use of the chainomatic specific gravity balance is convenient for 15 ml samples.

For viscous oils, the preferred method is ASTM D 70 and for solids the ASTM D 71 method is used.

If the residue, after concentrating and drying, is completely soluble in each of the three solvents, the density or the API gravity is determined. The second test will determine whether the sample is high or low gravity naphtha, gasoline, jet fuel, kerosene, gas oil, motor oil, fuel oil #1, fuel oil #2, or fuel oil #4. Table III shows the distinctive properties of each petroleum product.

Table III. Distinguishing Features of Petroleum Products

| | |
|---|---|
| Crude Oil | - most frequently sour, wide boiling range |
| High g. naphtha | - low sulfur |
| Low g. naphtha | - low sulfur |
| Gasoline | - lead, halogens (phosphorus or boron?) |
| Jet fuel | - low sulfur, API gravity - additives |
| Kerosene | - low sulfur, API gravity |
| Gas oil | - higher sulfur and API combination |
| Diesel oil | - similar to Kerosene, Fuel Oil #1 |
| White oil | - paraffinic (IR), colorless |
| Cutting oil | - glycerides, sulfur, (halogens), mineral oil |
| Motor oil | - metals (Zn), phosphorus, sulfur, additives, frictional properties low |
| Paraffin wax | - solid, paraffinic (IR) |
| White petroleum jelly | - partly soluble in hexane, in ether, and in chloroform |
| Grease | - metal soaps?, low frictional properties; hexane and ether insoluble, soluble in chloroform |
| Fuel oil #1 | - similar to Kerosene; low sulfur, API gravity |
| Fuel oil #2 | - Kinematic viscosity |
| Fuel oil #4 | - Kinematic viscosity |
| Fuel oil #5 | - Kinematic viscosity |
| Fuel oil #6 | - hexane and ether insoluble, soluble in chloroform, ratio of infrared absorbances |
| Asphalt (Blown or feed) | - hexane and ether insoluble, soluble in chloroform, ratio of infrared absorbances, since similar to Fuel Oil #6 |

Advantage can be taken of these properties in order to distinguish the products from each other.

Table IV groups four sets of petroleum products into similar API gravity ranges. Since the gravity alone will not be sufficient to produce distinctiveness, other properties are given to provide additional evidence for characterization.

Table IV. Petroleum Products with Similar API Gravity Ranges

| Product | Gravity API | Distillation iB.P.-eP. | Comment |
|---|---|---|---|
| High gravity naphtha | 45 - 75 | 95° - 206°F | |
| Low gravity naphtha | 30 - 53 | 160° - 410°F | |
| Gasoline | 58 - 62 | 96° - 408°F | lead, colored |
| High gravity naphtha | 45 - 75 | 95° - 206°F | S <0.02% |
| Low gravity naphtha | 30 - 53 | 160° - 410°F | S <0.02% |
| Jet fuel | 40 - 55 | 100° - 500°F | S <0.10% |
| Fuel oil #1 | >35 | 360° - 625°F | S = 0.1-0.5% |
| Kerosene | 40 - 46 | 355° - 575°F | S <.13% |
| Low gravity naphtha | 30 - 53 | 160° - 410°F | |
| Gas oil | 30 - 33 | 400° - 800°F | |
| Paraffin wax | 34 - 39 | MP = 147°-196°F | Paraffinic (IR) sol. in $CHCl_3$ |
| White oil | 29 - 32 | | Paraffinic (IR) |
| Motor oil | 24 - 30 | | P, S, Zn |
| Fuel oil #2 | >26 | 370° - 675°F (90%) | K. Vis. <4.3 High sulfur |
| Fuel oil #4 | 9 - 36 | 420° - 683°F | K. Vis. 32 - 81 High sulfur |

Therefore, the two naphthas and gasoline can be differentiated from each other by comparing the initial and final boiling points of the material. Jet fuel and gasoline are different in the end point and in the API gravity values. Jet fuel differs from the low gravity naphtha in the initial and final boiling point range as well as in the sulfur content. Kerosene is distinguishable from the naphtha and jet fuel in initial and final boiling points.

In some cases the sulfur and API gravity values will help in differentiation. Gas oil is distinguishable from the six petroleum products mentioned above in both API gravity and boiling range or sulfur values.

Motor oil is soluble in all three solvents, hexane, ether, and chloroform. It is characterized by a narrow range of API values. Motor oil differs from white oil, gas oil, and naphtha, having a higher initial boiling point. Indeed, the motor oil has a characteristic phosphorus to sulfur ratio of 0.5. Zinc is present at about 1/2 of the phosphorus value. High ash content is characteristic of motor oil and most greases.

Fuel oil #1 can be used as a diesel fuel, in which case amyl nitrate will be present. This product is quite similar to kerosene.

White oil is distinctively colorless. It is paraffinic as indicated by the infrared spectrum.

Fuel oils #1, #2, #4, and #5 show distinctive kinematic viscosity values at 100°F. Also, the latter three fuel oils have unusually high

sulfur values, and thus may be readily distinguished from the naphthas, gasoline, and jet fuel. The fuel oil API gravities are distinctly lower than the API gravities of naphthas, gasoline, and jet fuel.

Generally, crude oils contain mercaptans which can be detected by the use of the doctor test (6) involving the reaction of sodium plumbite and sulphur. The characteristic reaction of black precipitate shows the presence of mercaptans which are converted to the dialkyl disulfide and polysulfides.

Doctor Test

One hundred and twenty-five grams of sodium hydroxide are dissolved in one liter of distilled water. To the mixture, 60 grams of lead oxide are added. The entire mixture is shaken, permitted to stand for one day, and then filtered.

A 10 ml test sample is vigorously shaken in a test tube with 5 ml of the freshly filtered sodium plumbite solution. A pinch of sulfur is added and the contents are shaken vigorously for 15 seconds. Sufficient sulfur is added so that most of it floats at the interface of the two phases. If the mixture is discolored, the test is reported as positive. If the sulfur or the mixture remains unchanged or yellow, the test mixture is considered sweet or mercaptan-free.

In characterizing the crudes, their wide distillation range is a useful property.

Paraffin wax is identifiable as a colorless solid with a wide melting point range. It is soluble in hexane, in ether, and in chloroform. The infrared spectrum shows only long chain paraffins.

White petroleum jelly is only partially soluble in each of the three solvents. Its infrared spectrum shows strong paraffinic character and little or no aromatic character.

Grease, asphaltic material, and residual fuel oil #6 are characteristically insoluble in hexane and ether solvents. However, the three petroleum products are soluble in chloroform.

Greases are characterized by a high metals content. Metals such as lithium, sodium, calcium, barium, zinc or lead, may be present. When the metals are absent, the nitrogen content may be high. The grease will then be only partially soluble in chloroform. Thickeners may be graphic, silica, ureas, or ammeline. Silicones fluorocarbons, esters, or organic acid moiety, or lube oil may be present. The infrared spectra may indicate these groups.

The two remaining petroleum products, asphalts and fuel oil #6, have unusually low API gravity. These materials have usually higher sulfur values and high content of nickel and vanadium. They are higher boiling materials. These products are differentiated from one another and also identified by use of comparative ratios of infrared absorbances (12, 16), even though the products have similar infrared spectra. Three infrared absorbances are used to yield two ratios which provide

a linear relationship involving aromaticity, paraffinicity, and branching. This newly-developed tool shows excellent promise.

After the API gravity and solubility behavior have been determined, additional evidence for characterization of the unknown petroleum product may be obtained by determining the sulfur or distillation range values.

Determination of Sulfur

The determination of volatile organic sulfur compounds may be conducted in the manner described by Martin and Grant (18). A satisfactory procedure for the total organic sulfur, whether volatile or non-volatile, is that described by Belcher (4). The oxygen-bomb method of decomposition is used and the final, almost pure solution, is titrated with barium perchlorate-Thorin. In this method the evaluated sample sizes varied from 10 to 30 µg of organic sulfur. This method was selected after a lengthy study for completeness of decomposition, and colorimetric titration of numerous methods. Special procedures are given for interfering iodine and phosphorus. This method has been quite successful.

Determination of Distillation Ranges (1)

The distillation range of naphtha petroleum products is determined by the ASTM D 86-56, while the boiling range of the aromatics may be determined by the ASTM D 850. A special procedure, ASTM D 216, is highly recommended for very volatile naphthas. In the latter method

the apparatus is identical to ASTM D 86-56 except that a lower range thermometer is used. Also, there is a slight variation in procedure of the ASTM D 216-54 when compared to that of ASTM D 86-56.

The ASTM D 86 method of test is intended for use in the distillation of gasoline, naphtha, kerosene, and similar petroleum products. The initial boiling point is recorded as the reading of the distillation thermometer when the first drop falls from the end of the condenser. The end point is the highest thermometer reading observed during the distillation of the product under test. Appropriate distillation apparatus and directions for the method are described. (It should be recognized that evaporation and contamination in surface waters will affect the readings in all determinations listed).

The determination for the molecular weight is given below since this test is of value for low and high boiling petroleum products. The test is not necessary in most cases.

Determination of the Molecular Weight by the Rast Method (21)

About 50 mg of the dried, retrieved material is placed into a weighed, four-inch test tube. The weight is taken. About 500 mg of d-camphor is added and contents are weighed. Before heating, the test tube is stoppered. The contents are melted by placing the tube in a heated oil bath. A clear solution results. The tube is swirled to mix the contents as a clear solution. The mixture is heated no longer

than one minute and cooled. The solid is powdered. (This method may be replaced by the ebulloscopic or mass spectroscopic method for the volatile materials.)

The melting point of the mixture is determined in a melting point tube, using a thermometer which reads to 0.2°F. Melting points of several samples from the mixture are determined and the average value is calculated. The melting point of the original camphor is taken. The difference, $\Delta$, between these two temperatures is the depression of the melting point of the mixture.

The molecular weight is calculated from the following formula,

$$M = \frac{40 \times w \times 1000}{\Delta \cdot W}$$

in which w is the weight of the material, W is the weight of camphor, and 40 is the molecular freezing point depression constant for camphor.

If the unknown petroleum pollutant is found to be insoluble or partly soluble in chloroform, a melting point is determined for the material. Ammeline, ureas, and waxes are typical solids.

Determination of the Melting Point (1)

The determination of the melting point for petrolatum and for microcrystalline wax is the ASTM D 127-49. The ASTM petrolatum melting point is that temperature at which the material becomes fluid to drop from the thermometer.

ASTM D 87-57 describes the procedure for the determination of the melting point of paraffin wax. ASTM paraffin wax temperature is that temperature at which the melted wax first shows a minimum rate of temperature change when cooled under the prescribed conditions. A temperature versus time cooling curve is plotted from the periodic temperature readings. The minimum rate of temperature change is usually represented by a plateau in the cooling curve.

The API gravity and solubility studies will not yield sufficient information to characterize asphalt, fuel oil #6, or greases. These products are insoluble in ether and in hexane, but are soluble in chloroform. Greases are characterized by low frictional properties. Metals such as lithium, barium, zinc, or lead may be present in the greases. Since lube oils and fuel oils have distinctive viscosity (kinematic), this measurement is suggested. Such measurements will differentiate fuel oil #1, #2, #4, #5, and #6.

Determination of the Viscosity (1)

In Table V the wide range of viscosity of the petroleum products is illustrated.

Table V. Properties of Petroleum Products-Viscosities (23)

| Type of Oil | Viscosity Saybolt | | API |
|---|---|---|---|
| Natural gasoline | | | 76.5 |
| Gasoline | | | 57.0 |
| Water | | | 10.0 |
| Kerosene | | | 42.0 |
| Distillate | 37 at 100°F | | 35.0 |
| An average l, crude oil | 33 at 100°F | | 48.0 |
| Average crude oil | 40 at 100°F | | 40.0 |
| Average crude oil | 50 at 100°F | | 35.6 |
| An average h. crude oil | 60 at 100°F | | 32.6 |
| Wyo. crude oil | 40 at 100°F | | 36.4 |
| ASTM Fuel 3 (max. vis.) | 45 at 100°F | | 26.0 |
| ASTM Fuel 5 (min. vis.) | 50 at 100 | | 15.0 |
| SAE 10W lube | 10,000 at 0°F | 200 at 100°F | 31.0 |
| SAE 20W lube | 40,000 at 0°F | 320 at 100°F | 29.0 |
| Thin SAE 10 lube (100 V.I.) | 90 at 130°F | 160 at 100°F | 30.0 |
| Thin SAE 10 lube (0 V.I.) | 90 at 130°F | 180 at 100°F | 27.0 |
| Thin SAE 30 lube (100 V.I.) | 255 at 130°F | 70 at 210°F | 26.0 |
| Thin SAE 30 lube (0 V.I.) | 255 at 130°F | 58 at 210°F | 21.0 |
| ASTM Fuel 5 (Max. Vis.) or Fuel 6 (min. Vis.) | (Furol) 40 at 122°F | 800 at 100°F | 11.0 |
| Average SAE 50 lube (100 V.I.) | 90 at 210°F | 986 at 100°F | 25.0 |
| Average SAE 50 lube (0 V.I.) | 90 at 210°F | 2,115 at 100°F | 19.0 |
| Thick SAE 70 lube (100 V.I.) | 150 at 210°F | | 23.0 |
| Thick SAE 70 lube (0 V.I.) | 150 at 210°F | | |
| ASTM Fuel 6 | | | |
| Bunker C (max.) | (Furol) 300 at 122°F | | 8.0 |
| M.C. residium | 300 at 210°F | | 19.8 |
| Asphalt | (50 penetration) | | |

The API gravity is also given with the Saybolt viscosity for each petroleum product. It should be recognized that these are examples. As crude oils vary widely in composition and are subjected to different processes for manufacture of petroleum products, these figures will deviate strongly. However, a characteristic viscosimetric value may yield a clue as to the identity of the product type. Consideration of the API gravity, with sulfur values, infrared data, with boiling point range will facilitate the identification of the product.

Viscosity is the measure of the internal resistance of an oil to flow. Values are usually expressed as the number of seconds in time required for a certain volume of the oil under test to pass through a standard orifice under prescribed conditions. For kinematic viscosity the tentative method of test is ASTM D 445-53T. It is the absolute viscosity divided by the density, both obtained at the same temperature of determination. The unit of measurement is the centistokes. Conversion of the kinematic viscosity to Saybolt Universal Viscosity for 100° and 210°F values is provided in the conversion table included in ASTM D 446-53.

## IDENTIFICATION

The techniques and methods useful for the characterization of the numerous petroleum pollutants have been outlined. To further identify the petroleum pollutant, several additional analytical tools are available. These are principally infrared spectroscopy and gas chromatography.

A third method involves the analyses of trace metals and other minor constituents.

Gas Chromatography

Gas chromatography is one of the most efficient general methods for separating components in a mixture. However, the effectiveness of the chromatographic separation process is highly dependent upon use of the proper column. Important parameters that govern performance and resolution must be considered (8, 17).

Chromatographic Analyses

For the identity of classified, volatile petroleum products, such as naphthas, gasoline (24), jet fuel, and kerosene, it is highly recommended that the dried, recovered residual material be analyzed by gas chromatography. As volatility is a strong characteristic of the above products, a portion representing the volatiles of the gas chromatographic spectrum of the reference or known sample will be missing in the unknown petroleum sample which is exposed for long period. Time and temperature of the environment, as well as the fuel volatility, must be considered in matching the unknown with the reference sample. If the gas chromatogram of the unknown shows qualitative and quantitative match with the reference sample, except for reference peaks which represent compounds of high volatility or solubility in water, the two products can be judged as being from the same source.

The use of the gas chromatograph as a means to identify the heavier products, such as residual oils and asphalt, is limited. However, gas oils, paraffins, white oils, and motor oils can be identified by this method, if they are volatile under the condition of analysis.

Martin and Winters (19, 20) have developed a special method for determining saturates through $C_7$ and alkyl-benzenes through $C_{10}$ in crude oils. The hydrocarbons to be determined are separated from the crude oil with a packed prefractionator column, collected in a liquid nitrogen trap, and then released into either of two capillary columns through a stream splitter. Components through $C_7$ are well resolved in four hours on a 500-foot capillary column with 1-octadecene. Alkyl benzenes through $C_{10}$ are resolved on an 800-foot column coated with polyethylene glycol. Uncertainties in the results generally are less than 6% relative.

To characterize crude oils fully, detailed knowledge of composition is needed. Conventional methods involve analyzing narrow-boiling distillate fractions with a variety of techniques (B.P., R.I., U.V., etc.). Results are usually satisfactory, but analyses are prohibitively lengthy.

Packed columns have been used for determining individual components in crude oil but resolution is far from ideal. However, this method is accurate, detects trace components, and does not involve a prior distillation. Hydrocarbons of a selected boiling

range are separated from the crude oil by the prefractionator column and are collected in the liquid nitrogen trap. The prefractionator, a short packed gas chromatographic column, fractionates approximately by boiling point differences. After the desired boiling range fraction has been trapped, the prefractionator is bypassed by changing the position of the four-way valves. The trap is then warmed and the hydrocarbons are carried into the capillary column through the stream splitter. The individual components are detected by hydrogen-flame ionization as they emerge from the column. Volatile compounds remaining on the prefractionator are removed by back flushing. For determining hydrocarbons through $C_7$, a capillary column coated with 1-octadecene is used. For alkyl benzenes through $C_{10}$, a column coated with polyethylene glycol is used.

Hydrocarbons

The column is a 500 feet by 0.001 inch stainless steel capillary coated with 1-octadecene. All hydrocarbons through $C_7$ and 10 lowest boiling $C_8$ are well resolved, when the column is operated at 30°C with helium-exit flow of 0.85 ml per minute at a gauge pressure of 35 p.s.i. A temperature of 30°C gives optimum resolution. With a change of temperature on the octadecene column, the elution position of some hydrocarbons will change. An increase or decrease of only 3°C causes at least one pair of compounds to elute together. With an increase in temperature, cycloparaffins and aromatics are retained on the column longer relative to paraffins.

Alkyl benzenes through $C_{10}$

Determination of alkylbenzenes through $C_{10}$ is complicated by the presence of saturates that accompany the alkyl benzenes from the prefractionator column. The saturates would elute with the alkylbenzenes if a column separating compounds in order of the boiling point were used. However, interference is minimized by using a polar liquid phase that selectively retains alkylbenzenes while saturates of similar boiling points are separated first.

Good separations were obtained with an 800-foot by 0.01-inch column, coated with polyethylene glycol. This column has high separating power for individual alkylbenzenes and is selective in retaining the alkylbenzene past saturates. The column is operated at 60°C with a helium exit flow of 0.20 ml per minute at a gauge pressure of 45 p.s.i.

To perform the analysis, the double four-way valve is positioned so helium flows through the prefractionator into the liquid nitrogen trap. Helium flow is adjusted to 40 ml per minute.

The trap is immersed about two inches into liquid nitrogen. One to 20 ul of crude oil, which contains about 1.5% of one or more of the reference standards, is added. Elution is continued until the desired components are in the trap; the time needed must be precisely determined with prior runs. With this apparatus, four minutes are needed for elution of components through toluene: 6.5 minutes are needed for alkylbenzenes through 1, 3-dimethylbenzene: 15 minutes are needed for

alkylbenzenes through $C_9$. Similarly, gasoline and other volatile components may be analyzed and identified.

After the desired components have been typed, the position of the double four-way valve is switched. Helium pressure to the capillary column is adjusted. After equilibrium, current is applied to the stainless steel trap heater so that its portion of trap outside of liquid nitrogen reaches 130°C, after which the sample is introduced into the capillary column by removing the liquid nitrogen. Three seconds are required to vaporize the sample.

Results

Accuracy was estimated by analyzing synthetic blends made to simulate crude oil and by analyzing crude oils previously examined with packed columns. Average deviations from mean values are only 3% relative.

FIA method D 1319-61T (1)

This older method describes the procedure for the determination of the saturates, olefins, and aromatics (including aromatic olefins) in petroleum fractions that distill below 600°F. Gasoline is an example.

About 3/4 ml of sample containing traces of fluorescent dye (Sudan III) is introduced into a small glass adsorption column of 154 cm X 1.5 mm dimensions. Silica gel of 100 to 200 mesh size is used. When all the sample has been adsorbed on the gel, alcohol is added to desorb and develop the sample. The hydrocarbons are separated according to

their adsorption affinities into aromatics (including aromatics with olefinic side chains plus any sulfur, nitrogen, and oxygen compound), olefins, and saturates. The fluorescent dyes are also selectively separated with the sample fractions, and mark the boundaries of the aromatics, olefins, and saturates clearly visible under ultraviolet light. Ultraviolet light source with radiation at 3650A° is required. The volume percentage of each hydrocarbon type is determined by measuring the length of each zone in the long, narrow extension of the column. Reproducibility for experienced operators is about 3% for determining aromatics, olefins, and saturates.

A more defined characterization of the saturated fraction could be obtained by determination of the naphthenes in the saturated fraction. The ASTM D 2002-62T method covers the isolation of saturated hydrocarbons by shaking a measured amount of sample with a solution of $P_2O_5$ in concentrated $H_2SO_4$. The unreacted hydrocarbons, when separated, recovered and washed from the sulfonation acid, are representative of the saturates in the sample.

Infrared Analyses

A suitable tool for the identification of heavier petroleum products is the infrared spectrophotometer. As greases, heavy residual fuel oil, and asphalt are less volatile, the unknown infrared spectrum can be compared with the reference spectrum. If the unknown has been exposed unduly to environmental factors, such as air, sunlight, or

temperature, peroxidative (15) changes are considered. Useful information cannot be obtained from the infrared spectrum of the volatile petroleum products, such as naphthas and gasoline, unless an on-the-spot collection is made of the sample immediately following the spill.

Though each petroleum product is a mixture of numerous types of organic compounds, a peak-by-peak correlation qualitatively and quantitatively of an unknown sample against that of an authentic source sample is excellent evidence for identity. Certain group frequency bands permit the chemist to obtain useful information with reference to known functional group frequencies. These characteristic group frequencies may afford partial or complete characterization (5, 7, 25).

Infrared spectra may be obtained for gases, liquids, or solids. Because water sampling normally involves liquids or solids, the discussion on sample handling will involve the latter two items. Liquids may be examined in solution or neat. Liquids (neat) are tested between plates; the amount of material is several mg. Mobile liquids may be also handled in cells from 0.1 to 1 mm in thickness. However, when solutions are used, the selection of solvent is critical. The spectrum obtained from examination of a solution should be that of the solute except in regions where the solvent absorbs strongly.

For examining trace amounts of material, microcavity cells are used with a beam condenser. The cell may have a path length of 0.05 mm

and a capacity of 0.8 microliter. The solvent and sample should be dry and transparent in range of measurement. Carbon tetrachloride, carbon disulfide, and chloroform are the solvents frequently used. It is suggested that solutions analyzed with matched cells be dilute. Concentrated solutions will render useless the advantage of matched cells.

Solids are examined as a mull which are prepared by grinding several mg of the solid with a drop of Nujol. This mull is placed between two plates as a film. Solids may also be examined as discs made from 1 mg of material mixed, by vibration, with 100 mg of dried potassium bromide. In a die under pressure of about 30,000 lb per $in^2$ discs are pressed.

Before a sample is examined with a suitable infrared spectrometer, the following are required: (1) the instrument, e.g., Perkin Elmer 137, must be calibrated so that the absorption bands of the instrument's spectrum coincide with those established for a standard polystyrene film; (2) the sample to be examined should be free of moisture and solvents which may interfere with the unknown spectrum.

The two important areas for a preliminary examination are in the region below 7.4μ and in the 11.1 to 15.4μ region. Important absorption bands are interpreted after what has been observed in the high and low energy regions of the spectrum. The most frequently used band assignments for petroleum products derived directly from crude oil are given in Table IV.

Table VI. Most Frequently Used Band Assignments

| | | | | |
|---|---|---|---|---|
| Paraffins | (s)$CH_3$ | (a)$CH_3$ | (s)$CH_3$ | (a)$CH_3$ |
| | 3.38μ | 3.48μ | 6.8μ | 7.28μ |
| | (s)$CH_2$ | (a)$CH_2$ | | |
| | 3.42μ | 3.51μ | | |
| | | | $(CH_2)_4$ | |
| | | | 13.9μ | |
| Olefins | C=C | | | |
| | 6.0-6.1μ | Cis | 14.5μ | |
| | | Trans | 10.4μ | |
| | | Vinyl | 10μ, 11μ | |
| Aromatic | 3.23-3.33μ | 6.2-6.29μ; 6.7-6.76μ | | |
| | | | 11.1-15.4μ | |

The following functional groups should be considered in the more complex products, such as chemicals or peroxidized material: carbonyl, acidic, ester, ether, peroxido, hydroxyl, sulfoxides, sulfones, sulfides, phosphates, etc. Group frequency assignments are found in Bellamy (5) and other texts on infrared spectroscopy (7, 25).

To aid in identification, the dried grease is analyzed by infrared spectrometry and matched with the known or reference sample. The two spectra are compared. A match of peak-by-peak correlation is necessary for the entire spectrum, unless loss of certain group frequencies occurs due to solubilization of certain compounds in the aqueous medium or due to changes effected by the autoxidation process.

The nearly ash-free residue, after drying, is considered to be heavy residual fuel oil or asphalt when soluble only in chloroform. Measurement of the infrared absorbances at six group frequencies is made. These are 3050 $cm^{-1}$, 2925 $cm^{-1}$, 1600 $cm^{-1}$, 1375 $cm^{-1}$, 810 $cm^{-1}$, and 720 $cm^{-1}$. Absorbances are determined by the base-line technique. The length of the vertical line, which intersects the line tangential to the two proximate inflections, is measured. Ratio of intensity of the infrared absorption (RIA) at one frequency to that intensity of the absorption at another frequency is considered. These ratios are given in Table VII.

Table VII. Ratios of Infrared Absorbances of Commercial Asphalts & #6 Fuel Oils (16)

| RIA | Asphalt | #6 Fuel Oil |
|---|---|---|
| $\frac{720\ cm^{-1}}{1375\ cm^{-1}}$ | .28 | .20 |
| $\frac{3050\ cm^{-1}}{2925\ cm^{-1}}$ | .20 | .25 |
| $\frac{810\ cm^{-1}}{1375\ cm^{-1}}$ | .25 | .46 |
| $\frac{810\ cm^{-1}}{720\ cm^{-1}}$ | .87 | 2.42 |
| $\frac{1600\ cm^{-1}}{1375\ cm^{-1}}$ | .54 | .73 |
| $\frac{1600\ cm^{-1}}{720\ cm^{-1}}$ | 1.97 | 4.18 |

In addition, the average values of ratios of seven commercial asphalts and #6 fuel oils are given.

The #6 fuel oils are found to contain more aromatics that absorb at 800 $cm^{-1}$ than the asphaltic products, according to the plot of points $\frac{810\ cm^{-1}}{1375\ cm^{-1}}$ versus $\frac{810\ cm^{-1}}{720\ cm^{-1}}$. Asphalt ratios are located near the origin of the plot and have values less than 0.4 for the former ratio and less than 1.3 for the latter ratio. The heavy residual oils, or #6 fuel oils, lie on the same common line expressed by the equation $Y = 0.13\ X + 0.125$. In contrast to asphalts, residual oils are characterized by a smaller proportion of carbon methyls and methylene chains. The absorbance due to carbon methyl branching is about four times the absorbance due to the methylene chains.

The identity of the classified petroleum product, whether asphalt or residual oil, can be established by comparative evaluation of the above two ratios. Further, the identity of the unknown with the known is confirmed by comparing the remaining four ratios of the unknown with the known. All values should check.

Autoxidation (1b) of the residual oil in water at ambient temperatures will show increases in the ratios $\frac{1030\ cm^{-1}}{1375\ cm^{-1}}$, $\frac{1155\ cm^{-1}}{1375\ cm^{-1}}$, $\frac{1300\ cm^{-1}}{1375\ cm^{-1}}$, and $\frac{1695\ cm^{-1}}{1375\ cm^{-1}}$. These increases that occur within one week are due to increase formation of sulfoxides, alkyl ethers, secondary alcohols, and carbonyls. These small changes at the representative group frequencies should be considered when establishing the identity or source of pollutant with a fresh reference sample.

A point to consider in the evaluation of the vessels carrying or using foreign residual fuel oil is that this product normally contains less cracked stock than domestic fuel. The reason is that domestic residual fuel is the product obtained after numerous catalytic and thermal processes that are responsible for aromaticity and olefinic formation. Foreign residual fuel oils are products of straight-run distillation. The set of values may form a distinct linear relationship.

Trace Constituent Analyses

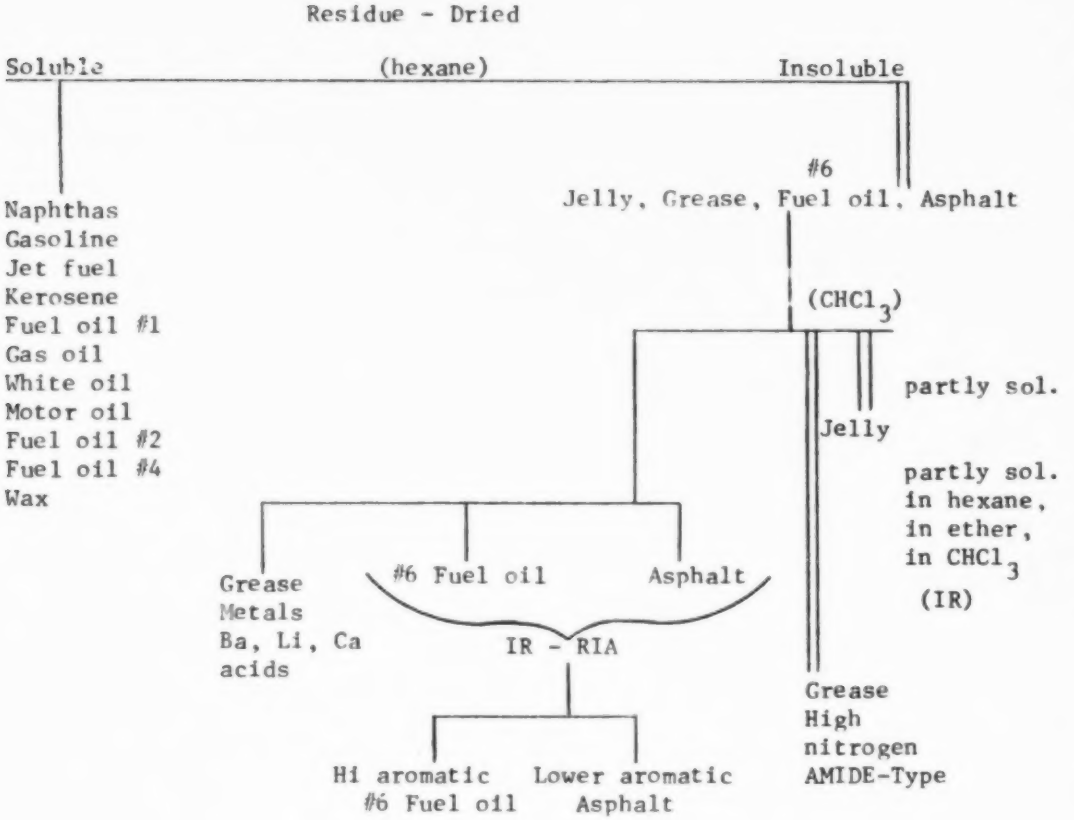
Many metals are found in trace quantities in petroleum (11). Some are in solution, some in suspension, and others are associated or chelated with the porphyrin molecules in petroleum. Generally, nickel and vanadium are present in highest quantity. The crude oil or residual fuel oil is washed, dry ashed, and analyzed by emission, absorption spectroscopy or by x-ray fluorescence.

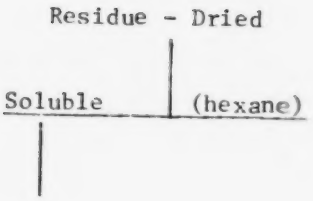
Ball et al. (2,3) made a comprehensive examination of a California crude oil containing appreciable quantities of nitrogen, sulfur, and oxygen. Concentrated in the asphalt fraction are the nitrogen compounds of high molecular weight. Small amounts are found in the distillates. These are suspected to be pyrroles, indoles, and carbazoles.

Of the oxygenated types of compounds, phenols and organic acids have been isolated. Investigation in this area will provide an addition to fundamental knowledge and an aid to economic processing

of the crude. If one applies a suitable method (13, 14) of minor constituent analyses, such information obtained will serve as an aid to identification. Types and amounts of acids, phenols, and mercaptans may serve to identify one crude oil from another.

Characterization Scheme






| | I.B.P.-e.P. | API - gravity | Comment |
|---|---|---|---|
| High gravity naphtha | 95° - 206°F | 45 - 75 | |
| Gasoline | 96° - 408°F | 58 - 62 | |
| Low gravity naphtha | 160° - 410°F | 30 - 52 | |
| Jet fuel | 100° - 500°F | 40 - 55 | |
| Kerosene | 355° - 575°F | 40 - 46 | |
| Fuel Oil #1 | 360° - 625°F | >35 | k. vis. |
| Gas oil | 400° - 800°F | 30 - 33 | |
| White oil | - | 29 - 32 | I.R.-paraffin |
| Motor oil | - | 24 - 30 | Zn, P, S |
| Fuel oil #2 | 370° - 625°F (90%) | >26 | k. vis. |
| Fuel oil #4 | 420° - 683°F | 9 - 36 | k. vis. |
| Wax | MP = 145°-190°F | 34 - 39 | Solid-IR paraffinic |

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